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A GENERAL METHOD OF CALCULATION IN KINETICS: THE METHOD OF AREAS. A METHOD OF APPROXIMATE EFFECTIVE AVERAGES.

BY RALPH E. DE LURY

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PART I. THEORETICAL

Introduction

In recent investigations in Chemical Kinetics there occur differential relations of the type,

$$\frac{dx}{dt} = K(A - x)^l\ (B - x)^m (C - x)^n \qquad (1)$$

where l, m, n, are positive or negative, and generally, though not always, integral. The problem is, in any case, to discover values of K, l, m, n that suit the particular reaction. The method of solving it, is to assume values of l, m, n, and then to examine whether for different values of t and the corresponding values of x the value of K is constant. But to do this we need the integral of the equation (1), and this integral can seldom be found in a form that lends itself to ready computation. In such cases methods of approximation have been employed. A short discussion of these methods will first be given, and this will be followed by an account of a method which, though implying in the end a mechanical quadrature, is on its theoretical side, rigorous. Further, the area as found by the planimeter or other means, represents a degree of accuracy quite as high as the experimental data warrant.

Methods that have been used

(I) *Integration by Partial Fractions*

In equation (1) assume l, m, n, to be positive integers; then,

$$K\int_0^t dt = \int_0^x \frac{dx}{(A-x)^l(B-x)^m(C-x)^n}. \qquad (2)$$

Therefore,

$$Kt = \int_0^x \left[\sum_{r=1}^{r=l} \frac{L_r}{(A-x)^r} + \sum_{r=1}^{r=m} \frac{M_r}{(B-x)^r} + \sum_{r=1}^{r=n} \frac{N_r}{(C-x)^r}\right]dx. \quad (3)$$

The integration yields $l + m + n - 3$ terms of the type,

$$-\frac{L_r}{r-1}\cdot\frac{1}{(A-x)^{r-1}}$$

and 3 terms such as,

$$L_1 . \log_e (A-x),$$

where L_r, M_r, N_r are functions of A, B, C, which can be determined, and hence K can be calculated.

When certain of the exponents l, m, n are negative the integral is evaluated in a somewhat similar manner.

This method is the one commonly employed and it implies that l, m, n are integers. The calculation is complicated when some or any of the positive exponents are at all large. For the case, $l = m = n = 1$, the values are easily found.[1]

(II) *Integration by Series*

Equation (2) may be written,

$$\mathrm{KA}^{l}\mathrm{B}^{m}\mathrm{C}^{n}\int_{0}^{t} dt = \int_{0}^{x}\left(1-\frac{x}{\mathrm{A}}\right)^{-l}\left(1-\frac{x}{\mathrm{B}}\right)^{-m}\left(1-\frac{x}{c}\right)^{-n} dx \qquad (4)$$

$$= \int_{0}^{x}\left[1 + x\left(\frac{l}{\mathrm{A}} + \frac{m}{\mathrm{B}} + \frac{n}{\mathrm{C}}\right) + x^2\left(\frac{l(l+1)}{2\mathrm{A}^2} + \frac{lm}{\mathrm{AB}} + \ldots\right) + \ldots\right]dx.$$

Therefore,

$$\mathrm{R} = \frac{x}{t}\left[1 + \frac{x}{2}\left(\frac{l}{\mathrm{A}} + \frac{m}{\mathrm{B}} + \frac{n}{\mathrm{C}}\right) + \frac{x^2}{3}\left(\frac{l(l+1)}{2\mathrm{A}^2} + \frac{lm}{\mathrm{AB}} + \ldots\right) + \ldots\right] \qquad (5)$$

where $\mathrm{R} = \mathrm{K}\ \mathrm{A}^{l}\ \mathrm{B}^{m}\ \mathrm{C}^{n}$, that is, the initial rate.

This series is only rapidly convergent when the ratios, $\frac{x}{\mathrm{A}}, \frac{x}{\mathrm{B}}, \frac{x}{\mathrm{C}}$, are small, and the calculation becomes tedious for values of these ratios greater than about one-fourth.

This method was used in calculating the values of R in the measurements of the rate of oxidation of potassium iodide by chromic acid.[2] The values of R are very close approximations. In the case where x was greatest (12 percent of the least concentration, A), an error of only 1 percent was made by neglecting the fourth term of the series in (5). When the coefficients of x^2, x^3, etc. are determined for any set of initial concentrations, the calculation of R (or K) is then very easy; this is therefore a good method to employ if there are many measurements in a set of experiments of the same initial concentrations.

(III) *Integration by Exponentials*

This method was introduced by Profs. W. Lash Miller and T. R. Rosebrugh.[3]

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[1] Fuhrmann: Zeit. phys. Chem., 4, 89 (1889).

[2] De Lury: Jour. Phys. Chem., 7, 239 (1903). Expts. 15, 16, 17, 25, 26, 27.

[3] Trans. Roy. Soc. Canada, Sec. 3, 73 (1903).

Equation (1) may be transformed into

$$K_1 t = \int_z^q e^{-z} z^{-l}\, dz + r/q^2 \int_z^q e^{-z} z^{2-l}\, dz$$

$$-s/q^3 \int_z^q e^{-z} z^{3-l}\, dz, \text{ etc.}, \qquad (6)$$

where K_1, q, r, s, and z are expressible in terms of A, B, C, l, m, n, and x.

Numerical values of certain of these functions have been computed; and by means of these tables the values of K can be calculated. The method is adapted to cases in which one concentration is smaller than the others and holds for all real values of the exponents.

(IV) *Direct Use of the Differential Equation*

W. C. Bray has recently described a method for the calculation of K from the differential equation.[1]

If, for example, the rate proceed in accordance with the equation:

$$dx/dt = K(A - x)\,(B - x)^2 \qquad (7)$$

he calculates values of k, defined by

$$dx/dt = k(A - x)$$

from successive pairs of x and t; and from them obtains K by the relation

$$K = \frac{k_1}{(B - x_1)^2} = \frac{k_2}{(B - x_2)^2} \qquad (8)$$

from which K can be calculated.

This method is particularly good when A is small relatively to the other concentrations. When there are several concentrations of about the same magnitude, and when the exponents are high, or are not integral, or are variable, difficulties arise in the use of this method; however, it should be of service in the study of complex reactions such as that treated by Bray in the paper cited.

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[1] Jour. Phys. Chem., 9, 573 (1905).

The above methods are somewhat limited in their application. The last three methods are approximate, but they will furnish for many cases approximations sufficiently close. The following method, general in its application, evades computations except those numerical reductions necessary for the construction of the curve, gives results as accurate as the results of the experiments sanction, and reveals readily the values of the exponents.

The Method of Areas[1]

(I) *General Case*

Suppose the reaction to take place according to the following equation,

$$\frac{dx}{dt} = K.F(x). \tag{9}$$

We have then,

$$\int_0^x dx = K\int_0^x F(x).dt$$

and therefore,

$$x = K\int_0^t F(x).dt. \tag{10}$$

If the curve F(x), t be plotted as in Fig. 1, where PQR is the curve F(x)' t we have,

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[1] This method suggested itself to the writer in April, 1905, while studying a case of complex oxidation: "The Rates of the Reactions in Solutions Containing Arsenious Acid, Potassium Iodide, Potassium Bichromate, and Sulphuric Acid," which is about to be published. While writing the present paper his attention was called to the article on *Mittlere Geschwindigkeit* by A. Fuhrmann (Zeit. phys. Chem., 4, 520 (1889); also, "Differential- und Integralrechnung" by the same author), who has given an excellent mathematical treatment of the subject of *average rate*. The writer knows of no instance where the ideas given in this paper have been applied in the study of Chemical Kinetics.

$$x = K \int_0^x F(x).dt$$

$$= K \times \text{area (OPQRT)}. \qquad (11)$$

By methods described below, the area (OPQRT) can be found accurately and hence the constant K can be calculated

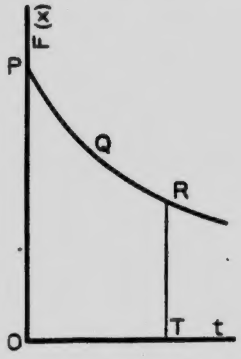

Fig. 1

for any assumed indices in the function, $F(x)$, and in this way the appropriate exponents can be determined.

Measurement of the Area

By using the experimental values of x, or preferably those taken from the x, t curve (as in Fig. 2), the function $F(x)$ can be calculated, and the curve $F(x)$, t (as in Fig. 1), can be plotted on section paper to a suitable scale (as large as possible). (*a*) The areas, $\int_0^x F(x).dt$, can then be quickly found by means of a planimeter. A good instrument will enable the operator to find the areas in question as accurately as the curve can be plotted (see Table VII, Part II). If a planimeter be not available the area may be calculated by employing certain approximate formulas for the area.

(*b*) By regarding the area as made up of a series of trapeziums of equal base, Δt, the area is expressed approximately thus,

$$\text{Area} = \Delta t(F_0 + F_1 + F_2 + \ldots\ldots + F_n) - \Delta t.\,\frac{F_0 + F_n}{2} \qquad (12)$$

where F_0, F_1, F_2, ...F_n, are the values of $F(x)$ when $t = 0$, Δt, $2\Delta t$,...$n\Delta t$. This formula is easily applied and, in general, gives close approximations without taking n very large.

(*c*) Some of "Simpson's Rules"[1] may be applied, or the squares of the section paper may be counted, or if the paper is sufficiently heavy the areas may be found by weighing.

Reverse or Successive Reactions

Suppose we have,

$$\frac{dx}{dt} = K_1.F_1(x) \pm K_2.F_2(x) \qquad (13)$$

then,

$$x = K_1\int_0^x F_1(x).\,dt \pm K_2\int_0^x F_2(x).dt. \qquad (14)$$

This is the general relation showing the progress of a reaction. In many cases the amount of change due to reverse or successive reactions is negligible; sometimes also there are instantaneous successive reactions: in such cases equation (10) would be used in place of equation (14). When, however, the change due to reverse or successive reactions is not negligible, by plotting $F_1(x)$ and $F_2(x)$, the values of K_1 and K_2 can be found by means of equation (14), any two experimental values of x with their corresponding measured areas being used.

Equation (14) generally takes some such form as,

$$x = K_1\int_0^x (A - x)^l(B - x)^m.dt - K_2\int_0^x (C - x)^n(D - x)^r.dt. \qquad (15)$$

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[1] See Williamson's Integral Calculus, p. 212.

It may be possible to determine one of the constants by choosing conditions such that the amount of change due to the other rate is negligible.[2] In many cases, however, this is not necessary, as equation (15) is easily applied.

(II) *Special Case*: $F(x) = A - x$

Let equation (10) take the form,

$$x = K\int_0^x (A - x).dt. \qquad (16)$$

Then,

$$x = K(At - \int_0^x x.dt)$$

$$= K.\left\{ \text{area (OPQT)} - \text{area (OSRT)} \right\}$$

$$= K. \text{ area (OPQRS)} \qquad (17)$$

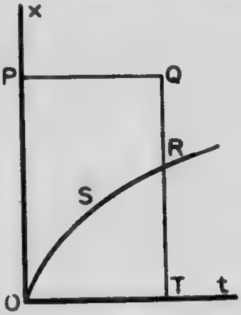

Fig. 2

where ORS is the curve x, t (Fig. 2), and OP = A.
Also,

$$\frac{x}{t} = K(A - \frac{1}{t}\int_0^x x.dt) \qquad (18)$$

where $\frac{x}{t}$ is the *average rate* during the interval . = o to $t = t$,

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[1] As in the case of iodide oxidation by arsenic acid : See Part II, Table I, for applications to this case.

and $\frac{1}{t}\int_0^t x.dt$ is the *effective average* value of $A - x$, that is, the effective average concentration of the chemical represented by A. Writing X for the effective average value of x that is, for $\frac{1}{t}\int_0^t x.dt$, we have,

$$\frac{x}{t} = K.(A - X). \tag{19}$$

(III) *Approximate Treatment: The Method of Approximate Effective Averages*

By extending the idea of effective averages a useful approximate formula is obtained as follows: If the reaction be represented by the equation,

$$\frac{dx}{dt} = K(A - x)(B - x)^m(C - x)^n \tag{20}$$

where B and C are large relatively to A, we have as a first approximation

$$\frac{x}{t} = K(A - X)\ (B - \frac{x}{2})^m\ (C - \frac{x}{2})^n \tag{21}$$

where X, as used above, has the value $\frac{1}{t}\int_0^t x.dt$. A much closer approximation is furnished by the following equation,

$$\frac{x}{t} = K(A - X)\ (B - X)^m\ (C - X)^n \tag{22}$$

where $A - X$, $B - X$ $C - X$, are *approximate effective average concentrations.* Under certain conditions equation (22) is a very close approximation (see Tables of Part II). The smaller the value of $m + n$ the closer the approximation; it is therefore very close when some of the exponents are negative. The difference between (22) and the exact equation (10) cannot be easily expressed mathematically.

(IV) *Application of the Above Methods to the Determination of the Exponents*

(*a*) Equation (22) may be employed in the form,

$$0 = \log K + \log (A - X) + m.\log (B - X) + n.\log (C - X) - \log \frac{x}{t}. \quad (23)$$

By using a sufficient number of values of x and t, the numbers K, m, n, may be calculated approximately.

(*b*) For any assumed exponents, equation (10) can be easily tested. $F(x)$ is calculated by logarithms and if these be put down systematically it will be an easy matter to calculate this function for various sets of exponents. However, the following method may be employed:

Suppose,

$$dx = K.f_1(x).f_2(x) \quad (24)$$

where $f_1(x)$ and $f_2(x)$ are functions of x. If $f_2(x)$ be plotted and $f_1(x)$ be a simple function (such as $A - x$), we have as a close approximation,

$$x = f_1(X).\int_0^x f_2(x).dt. \quad (25)$$

For example, if,

$$x = K.\int_0^x (A - x)^l \, (B - x)^m \, (C - x)^n . \, dt$$

we have approximately,

$$x = K.(A - X)^r \int_0^x (A - x)^{l-r} \, (B - x)^m \, (C - x)^n . \, dt \quad (26)$$

where r is supposed small (*e.g.*, $r = 1$). So that if the function had been plotted for the exponents $l - r$, m, n the values of $K(A - x)^r$ and hence of K can be found very closely by means of equation (26). This approximation will be of use in tracing the change in r where r is variable, as in the case of iodide oxidized by chromic acid mentioned above).

PART II. PRACTICAL APPLICATIONS

In the following applications of the foregoing principles, the curves used in measuring the areas were plotted to a suitable scale on millimeter section paper. The areas were measured by means of a planimeter, the arm being adjusted so that a reading of 1000 corresponded to 100 square centimeters. No difficulty was experienced in getting duplicate readings to agree (see Table VII). These readings were then reduced to the proper unit.

(*I*) *Mr. Roebuck's measurements on the Rates of the Reactions in Solutions containing Arsenious, Arsenic, and Sulphuric Acids, Iodine and Iodide.*[1] (Table I).

(*A*) *Comparison of Different Methods of Calculation*

This case is chosen as it affords a ready means of comparing the results of several methods of calculation, namely, the exponential method (employed by Roebuck in his original paper), Bray's method of employing the differential equation, the method of areas, and the method of approximate effective averages.

When iodide is oxidized by arsenic acid, the arsenious acid and triiodide formed react reversely. According to Roebuck, the law governing the reaction (apart from a slight deviation in the exponents of the concentrations of iodide [illegible] sulphuric acid) is as follows,

$$\frac{dx}{dt} = K_1(C-x)(D-x)(E-x) - K_2x^2(C-x)^{-2}(D-x)^{-1}, \qquad (27)$$

where x denotes the amount of triiodide, and therefore the amount of arsenious acid formed, and C, D, E denote respectively the amounts of potassium iodide, sulphuric acid and arsenic acid initially present.

For this case then, equation (14) assumes the form:

$$x = K_1\int_0^x F_1(x).dt - K_2\int_0^x F_2(x).dt$$

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[1] Roebuck: Jour. Phys. Chem., 6, 365 (1902); 9, 727 (1905). See also Bray: Ibid., 9, 573 (1905).

$$= K_1 \int_0^x (C - x)(D - x)(E - x) dt$$

$$- K_2 . \int_0^x x^2 . (C - x)^{-1} (D - x)^{-1} dt. \qquad (28)$$

In Roebuck's notation, K_1 is $k_5 . V^{-3}$, and K_2 is $k_3 . V$, where V is the volume in litres.

(a) *Assuming* $K_2 \int_0^x F_2 . dt = o.$

If we neglect the second term (representing the rate of oxidation of arsenious acid by triiodide) we may calculate k_5, which will then, of course, vary (in most of Roebuck's measurements this variation is negligible), by means of the equation,

$$x = k_5 . V^{-3} . \int_0^x (C - x)(D - x)(E - x) dt \qquad (29)$$

or approximately (see equation (22)),

$$x = k_5 . V^{-3} t (C - X)(D - X)(E - X) \qquad (30)$$

where $X = \frac{1}{t} \int_0^x x . dt$, that is, the *effective average* value of x for the interval t.

The curves $F_1(x), t$ and x, t were plotted (as in Fig. 3), the areas, $\int_0^x F_1(x) . dt$ and $\int_0^x x . dt$ measured, and the values of k_5 calculated employing equations (29) and (30). The constants thus calculated are denoted by $(29), k_5$ and $(30), k_5$ in the following table. In this table the values of t, x, and k_5 are taken directly from Roebuck's Table XXVIII. The values of $(\text{dif}), k_5$, that is, the constants calculated by using the differential equation (see equation (8)), are taken from Bray's Table XXVIII.

(*b*) *Assuming* $k_3 = 0.28$

The constant $(31),k_5$ is calculated from equation (28), assuming the value of k_3 to be 0.28 (as Bray does in calculating $(\text{dif}),k_5$). For making this calculation the curve $F_2(x),t$ was plotted, and from the areas measured, $(31),k_5$ was obtained by means of the relation,

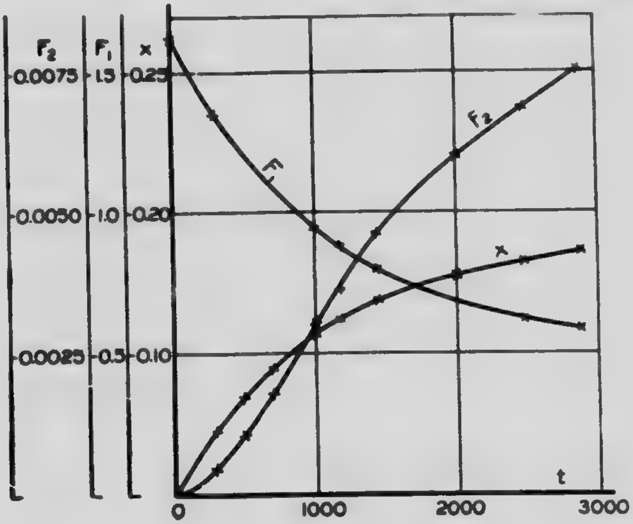

Fig. 3

$$k_5 = (29),k_5 \cdot \frac{x + k_3 . V . \int_{t_0}^{t_x} F_2(x).dt}{x} \qquad (31)$$

(*c*) *Comparison of the "Constants"*

It will be seen from Table XXVIII that $(30),k_5$ is practically identical with the "constant" $(29),k_5$, while k_5 which was calculated by the exponential method grows smaller and smaller as x increases, as would be expected. A comparison of $(31),k_5$ and $(\text{dif}),k_5$ shows the latter to be somewhat erratic. The reason that the various approximations are so close to those calculated by the area method, is that C and D are much larger (seven times) than E.

(*B*) *Calculation of* K_1 *and* K_2 *Assuming the Exponents as in Equation* (28)

K_1 and K_2 were calculated from equation (28), the two values of x necessary in each case being taken from successive measurements in Roebuck's Table XXVIII.

From these numbers the constants, (28),k_5 and (28),k_3 were calculated from the relations, $K_1 = (28), k_5.V^{-3}$ and $K_2 = (28), k_3.V$. The value of (28),k_5 is the same as the initial value of (29),k_5 in calculating which the other rate was neglected: this is natural, as of course the other rate is practically zero at the beginning of the experiment. The constant, (28),k_3, is found to be 0.049, that is, about one-sixth the value of k_3 (viz., 0.28) found in experiments where the concentrations were very different from those of Table XXVIII. This points to a change in the constant itself or (as Roebuck supposed) to a change in the values of the exponents, and shows that the *two* assumptions, viz., that $k_3 = 0.28$, and that the exponents are the same as in equation (28), cannot both be true for concentrations such as those used in the experiments of Roebuck's Table XXVIII. It is consequently not surprising to find that the constants (31),k_5 and (dif),k_5 rise in value—either the correction for the rate of oxidation of arsenious acid by triiodide is too great, or the exponents of the other rate are too low. It is also not surprising that $\frac{k_3}{k_5}$, calculated[1] on the above *two* assumptions, is five or six times greater than the equilibrium constant, K_6,[2] which is calculated on the one assumption. Since, moreover, the numbers, (28),k_3 and (28),k_5 (in the following Table I), are calculated on the *one* assumption that the exponents are the same as in equation (28), their quotient (the equilibrium constant) should be the same as K_6[2] of Roebuck's Table XXXIII, which was calculated on the same assumption, the concentrations being about the same in the two tables. Such we find to be the case, for,

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[1] Roebuck: Loc. cit., p. 396, $\frac{k_3}{k_5} = \frac{0.28}{3.26 \times 10^{-7}} = 8.6 \times 10^5$, or better, $\frac{0.28}{3.7 \times 10^{-7}}$.

[2] Ibid: Table XXXIII, p. 395.

$$\frac{(28),k_2}{(28),k_6} = \frac{0.049}{3.7 \times 10^{-7}} = 1.3 \times 10^5\text{; and } K_e = 1.5 \times 10^5.$$

It is probable, however, that this value of the equilibrium constant is not correct, since the exponents of the equation (28) do not hold for the concentrations of the table from which it is calculated (see Roebuck's second paper).

(*C*) *Mr. Clark's Work on the Rate of Oxidation of Iodide by Bromate in Acid Solution*

Mr. R. H. Clark gives, in a paper about to be published, the following equation to represent the rate of oxidation of iodide by bromate in acid solution,

$$\frac{dx}{dt} = K(A - x)\,(B - x)\,(C - x)^2 \qquad (32)$$

where A, B, and C denote the amounts (in equivalents) of bromate, iodide and acid respectively, initially present, and x denotes the amount (in the same unit) of iodide oxidized in t minutes. Several investigators (see the above-mentioned paper) have studied this reaction, but have not interpreted their measurements as in (32). Some of their measurements have been recalculated, employing the approximate equation (see equation (22)),

$$x = Kt(A - X)\,(B - X)\,(C - X)^2 \qquad (33)$$

and also by using the exact relation,

$$\begin{aligned} x &= K.\int_0^x F(x).dt \\ &= K\int_0^x (A - x)\,(B - x)\,(C - x)^2.dt. \qquad (34) \end{aligned}$$

Most of the measurements (as in Tables II–VI) could not be recalculated by any of the methods of approximation described in the preceding part, and since the reaction is of the fourth

TABLE I

C, 2.270; D, 2.293; E, 0.310: V, 0.155

t	x	$k_5 \cdot 10^7$	$\frac{1}{t}\int_0^x x.dt$	(30), $k_5 \cdot 10^7$	$F_1(x)$	$\int_0^x F_1(x).dt$	(29), $k_5 \cdot 10^7$	$F_2(x)$	$\int_0^x F_2(x).dt$	(31), $k_5 \cdot 10^7$	(dif), $k_5 \cdot 10^7$	K_1	(28), $k_5 \cdot 10^7$	K_2	(28), k_3
296	0.434	3.62	0.024	3.74	1.339	434	3.72	0.00040	0.035	3.84	4.0	—	—	—	—
994	0.113	3.22	0.064	3.50	0.926	1214	3.47	0.00303	1.15	5.00	5.6	0.000101	3.76	0.0073	0.047
1177	0.122	3.17	0.072	3.32	0.879	1378	3.30	0.00359	1.79	5.41	4.9	0.000105	3.91	0.0081	0.052
1432	0.137	3.07	0.084	3.26	0.795	1592	3.20	0.00460	2.83	6.14	6.5	0.000095	3.53	0.0078	0.050
2480	0.164	2.61	0.112.	2.64	0.614	2316	2 64	0.00684	8.92	8.89	9.7	0.000099	3.68	0.0076	0.049
2880	0.171	2.34	0.120	2.49	0.579	2562	2.49	0.00752	11.82	9.98	9.8	0.000096	3.57	0.0072	0.047
											Avg.	0.00010	3.7	0.0076	0.049

K_1 was calculated, using equation (28); then K_2 was calculated, using the average value of K_1.

Equilibrium constant $K_e = \frac{k_3}{k_5} = \frac{0.049}{3.7 \times 10^{-7}} = 1.3 \times 10^5$.

order the method of integrating by partial fractions would lead to rather involved computation.

In Tables II–VI are given recalculations of some of Magnanini's measurements (see Mr. Clark's paper for others). These tables are chosen as they afford a means of comparing the approximate equation (33) with the exact equation (34); the constants as calculated by these methods are denoted in the tables by (33), K and (34), K respectively. X is written for the effective average value of x, that is, for $\frac{1}{t}\int_0^t x.dt$, and $F(x)$, as in (34), is written for $(A - x)(B - x)(C - x)^2$.

The fall in the constant (34),K in the earlier tables, as also the change in this "constant" from table to table, is possibly due to the fact that A, B, and C are the analytical and not the ionic concentrations.

TABLE II

A, 11.11; B, 7.41; C, 12.96; Vol. 10 cc.

t	x	$\int_0^t x dt$	X	(33),K.10^7	$10^{-2}.F(x)$	$10^{-3}\int_0^t F(x).dt$	(34),K.10^7
5	0.83	2.40	0.48	144	99.8	58.3	142
12	1.44	10.8	0.90	124	77.6	121	119
13	1.46	12.4	0.95	119	75.9	126	116
21	1.84	25.2	1.20	113	63.9	183	100
25	2.05	32.0	1.28	100	57.9	207	99
41	2.73	70.0	1.71	98	41.3	283	93
52	2.97	101.6	1.96	94	38.3	326	91
84	3.69	209.2	2.49	94	23.7	419	88
91	3.81	236.0	2.59	95	22.1	431	89
175	4.82	608.0	3.47	102	10.8	560	86

TABLE III

A, 11.11; B, 7.41; C, 24.07; Vol. 10 cc.

t	x	$\int_0^x x\,dt$	X	(33), $K.10^7$	$10^{-2}.F(x)$	$10^{-3}\int_0^x F(x).dt$	(34), $K.10^7$
2	0.82	0.88	0.44	99	477	82.5	99
3	1.05	1.68	0.56	88	367	120.5	87
9	2.35	12.40	1.38	86	339	279	84
15	3.27	29.04	1.94	89	209	384	85
17	3.38	35.52	2.09	87	141	412	81
28	4.38	78.4	2.80	90	133	519	84
31	4.50	91.7	2.96	90	77.3	540	83
35	4.68	110.3	3.15	90	73.7	557	84
40	5.10	134.6	3.36	95	66.0	593	86

TABLE IV

A, 11.11; B, 7.41; C, 35.18; Vol. 10 cc.

t	x	$\int_0^x x\,dt$	X	(33), $K.10^7$	$10^{-2}.F(x)$	$10^{-3}\int_0^x F(x).dt$	(34), $K.10^7$
2	1.43	1.56	0.78	88	658	169	85
6	2.98	10.84	1.61	87	373	361	83
12	4.19	32.32	2.69	84	215	523	80
17	4.93	55.4	3.26	87	140	615	80
18	5.06	60.4	3.36	87	129	630	80
20	5.28	70.4	3.52	88	111	654	81

TABLE V

A, 11.11; B, 7.41; C, 46.29; Vol. 10 cc.

t	x	$\int_0^x x\,dt$	X	(33), $K.10^7$	$10^{-2}.F(x)$	$10^{-3}\int_0^x F(x).dt$	(34), $K.10^7$
2	2.03	2.24	1.12	79	957	245	83
4	3.17	7.76	1.94	80	626	385	82
6	3.93	14.56	2.43	79	448	486	81
8	4.52	23.0	2.88	81	331	558	81
10	4.90	32.7	3.27	81	267	615	80
11	5.08	37.5	3.41	82	239	640	79

TABLE VI

A, 11.11; B, 7.41; C, 57.4; Vol. 10 cc.

t	x	$\int_0^t x dt$	X	(33),K.10^3	10^{-3}.F(x)	$10^{-3}\int_0^t$ F(x).dt	(34),K.10^3
2	2.55	2.92	1.46	70	1251	379	68
4	3.94	9.56	2.78	75	711	565	70
6	4.72	18.1	3.01	74	477	675	70
7	5.15	23.2	(3.71)	(79)	368	716	72
8	5.33	28.1	3.51	77	326	743	72

In all of the above tables, it will be seen that for small values of x, the "constant" (33),K and (34),K are practically equal. As x increases, however, the former gradually grows larger than the true "constant" (34),K, showing that the approximate value of x, namely,

$$Kt(A - X)(B - X)(C - X)^2, \qquad \text{(from equation (33))}$$

gradually falls off from the true value,

$$K\int_0^x (A - x)(B - x)(C - x)^2.dt, \qquad \text{(from equation (34))}$$

as x increases. The difference between these expressions becomes less and less as C is increased, until when C becomes four or five times the value of A, as in Tables IV and V, the two expressions become nearly equal; this is shown by the fact that (33) K and (34),K are nearly equal in these tables. Hence in general we have as a close approximation, if $\frac{x}{A}$ be not greater than $^1/_2$,

$$x = K.\int_0^x (A - x)^2 dt = Kt(A - X)^2. \tag{35}$$

(*D*) *Test of the Accuracy of the Method of Areas, and the Method of Approximate Effective Averages*

The approximation (35) may be tested by assuming values of K,A,x, and the consequent values of t, and constructing the two necessary curves: assuming $K = 1$, $A = 10$, and for x the values 1, 2, 3, 4, 5, 6, the values of (from the equation $t = \frac{1}{10 - x} - \frac{1}{10}$) become $\frac{1}{90}, \frac{2}{80}, \frac{3}{70}, \frac{4}{60}, \frac{5}{50}, \frac{6}{40}$, respectively. With these values of x and t, the curves x, t and $(A - x)^2, t$ were plotted and the two expressions for x in equation (35) were calculated from the measurements of the areas $\int_0^x x.dt$ and $\int_0^x (A - x)^2.d$ as made by the planimeter. Under the word "Reading" are given duplicate readings of the planimeter for the areas in question (Table VI), and X has it's former meaning, namely, $\frac{1}{t}.\int_0^t x.dt$. The areas are expressed in the proper unit.

TABLE VII

t	x	Reading	$\int_0^x xdt$	X	$t(10 - X)^2$	Reading	$\int_0^x (10 - x)^2 dt$
0.0111	1.00	23; 23	0.00575	0.518	1.00	397; 396	0.99
0.0250	2.00	104; 103	0.0260	1.04	2.01	801; 802	2.00
0.0428	3.00	284; 283	0.0707	1.65	2.98	1198; 1199	3.00
0.0667	4.00	624; 626	0.156	2.34	3.91	1605; 1606	4.01
0.1000	5.00	1224; 1226	0.306	3.06	4.82	2005; 2005	5.01
0.1500	6.00	2332; 2330	0.583	3.89	5.60	2404; 2401	6.00

A comparison of the duplicate readings shows how closely areas can be measured by means of the planimeter: it is evident that these measurements can be made far more closely than a chemical analysis is usually made. Since x and $\int_0^x (10 - x)^2.dt$ are identical, the exactness of the method of areas can not be doubted. The value of the approximation,

$t(10 - X)^2$, differs from x by less than 4 percent when x is 5. It is evident from this, that equation (19) is applicable to the first half of bi-molecular reactions (and consequently to reactions of a higher order when all the concentrations but two, linearly involved, are practically non-variant). Hence in such cases equations (20) and (23) may be employed to calculate the values of the constant and the exponents, and where a deviation occurs in an exponent, to trace this variation. If desirable, a correction can be made by estimating the percentage error.

The above examples are sufficient to show the applicability of the Method of Areas and the Method of Approximate Effective Averages. At present I am employing these methods in the study of some cases of complex oxidation, and also in the recalculation of some kinetic measurements which have appeared in the chemical journals.

Summary

I. An outline of the methods that have been used in the computations occurring in the study of Chemical Kinetics, is given.

II. A "*Method of Areas*" is described. The Kinetic Equation is used in the following form,

$$x = K.\int_0^x F(x).dt \quad .$$

and in the case of reverse or successive reactions, in the form,

$$x = K_1.\int_0^x F_1(x).dt \pm K_2.\int_0^x F_2(x).dt.$$

The curve $F(x)$, t is plotted, the areas $\int_0^x F(x).dt$ are then measured by means of a planimeter, and the values of K are calculated from the values of x, and thus the correctness of the assumed function, F(x), is tested. The areas can be measured as accurately as the experimental data will warrant.

III. A "*Method of Approximate Effective Averages*" is described. The Kinetic Equation is used in the form,

$$\frac{x}{t} = \mathrm{K}\left(\mathrm{A} - \frac{1}{t}\int_0^x x.dt\right)^l \left(\mathrm{B} - \frac{1}{t}\int_0^x x.dt\right)^m,$$

which is a close approximation under certain conditions. This equation may be used in the following form to calculate approximately the values of K, l, m,.. by taking a sufficient number of values of x,

$$0 = \log \mathrm{K} - l.\log\left(\mathrm{A} - \frac{1}{t}\int_0^x x.dt\right)$$
$$- m.\log\left(\mathrm{B} - \frac{1}{t}\int_0^x x.dt\right) - \ldots - \log\frac{x}{t}.$$

The following equation may be used in some cases in tracing the variation in an exponent (r varying),

$$x = \mathrm{K}\left(\mathrm{A} - \frac{1}{t}\int_0^x x dt\right)^r \int_0^x (\mathrm{A} - x)^{l-r}\,(\mathrm{B} - x)^m \ldots dt.$$

IV. Some examples showing the applicability and accuracy of the above methods are given.

I am glad of this opportunity of expressing my gratitude to Professor W. Lash Miller. Without the training and help I have received from him, the above problems would doubtless never have occurred to me.

University of Toronto,
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